Amine-buffered Phase Separating Tetraethoxysilane–Water Binary Mixture: A Simple Precursor of Sol–Gel Derived Monolithic Silica Gels and Glasses

Shungo Kuwatani, Ryohei Maehana, Koichi Kajihara,* and Kiyoshi Kanamura
*Department of Applied Chemistry, Graduate School of Urban Environmental Sciences,
Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397*

(Received March 30, 2010; CL-100305; E-mail: kkaji@tmu.ac.jp)

Amines are used as pH control agents to form macroporous silica gels utilizing macroscopic phase separation of acid-catalyzed tetraethoxysilane–water binary mixture. The wide pK_a variety of amines from basic to acidic regions is suitable to buffer the solution at neutral pH range, at which the phase separation becomes prominent. This method allows monolithic silica gels and glasses to be prepared reproducibly from alkoxide-based solutions with minimal use of pH control agents.

Silica glass is important as an optical material for various extreme conditions such as fiber telecommunication, optical monitoring in nuclear plants, and deep-ultraviolet (DUV, $\lambda \lesssim 300\,nm$) excimer laser photolithography because of its excellent transparency from infrared to DUV spectral regions, good radiation hardness, and high chemical stability. The sol–gel method[1] is a wet-chemical process widely used to obtain silica gels, which are consolidated into glasses at relatively low temperature ($\lesssim 1400\,°C$). However, it is difficult to form crack-free monolithic silica glasses from alkoxide-based wet gels because they are usually nano- or mesoporous and the capillary pressure induced during drying of the pore liquid often causes fracture.[2–9] The fracture is suppressed by forming macropores, and in alkoxide-based systems it can be realized by inducing macroscopic phase separation in parallel with gelation.[10–14] Recently, we found a route to cause the macroscopic phase separation in tetraethoxysilane (TEOS)–water binary mixture[15,16] free from additives that promote the phase separation, such as organic polymers,[10,11] polar solvents,[12] concentrated strong acids,[13] and organically modified silanes.[14] The key technique is two-step mixing of TEOS and water. In the first mixing step, TEOS is partially hydrolyzed under acidic conditions at water to TEOS molar ratios of ca. 2. In the second mixing step, aqueous solution of a Brønsted base is added and the resultant pH increase enhances the polycondensation of silica oligomers while suppressing the hydrolysis of residual ethoxy groups. This procedure forms hydrophobic silica oligomers modified by ethoxy groups in hydrophilic solvent mixture consisting of water and ethanol and leads to the phase separation.

In previous reports,[15,16] solution pH after the second mixing was stabilized at a weakly acidic pH range by adding ammonium acetate and forming an acetate-based buffer system. However, pK_a values of conventional carboxylic acids are less than 5, making it difficult to buffer the solution at $pH \approx 7$, at which the hydrolysis is expected to be the slowest.[17]

In this study we employed amines as Brønsted bases. In sol–gel reactions, amines like ammonia are usually used to turn solutions basic. However, amines can be neutral or even acidic by introducing electron-withdrawing groups to the amine

nitrogen. Furthermore, organic amines are free from elements to give solid oxides and can be removed during sintering. We show that such properties of amines are useful to buffer gelling solutions at neutral pH range and that monolithic macroporous silica gels suitable as precursors of silica glasses are obtained reproducibly with minimal use of amines with $pK_a \approx 7$.

Ethylenediamine ($pK_{a1} = 9.9$, $pK_{a2} = 7.1$) and imidazole ($pK_a = 7.0$) were selected as model amines. Ethylenediamine has an additional advantage that it consumes multiple (two) protons per molecule. TEOS ($Si(OC_2H_5)_4$, Shin-Etsu Chemical Co., Ltd.) was mixed with a dilute aqueous solution of nitric acid. The mixture (molar ratio $TEOS:H_2O:HNO_3 = 1:x_1:0.002$) was stirred vigorously for 1 h at 20 °C to obtain a clear solution. Then an aqueous solution of a Brønsted base ($H_2O:base = x_2:y$) was added. The final solution composition was $TEOS:H_2O:HNO_3:base = 1:10(=x_1 + x_2):0.002:y$. The gelation time ($t_g$) was defined as the moment at which the solution lost the macroscopic fluidity and recorded as the time delay from the second mixing. The phase separation time (t_{ps}) was similarly defined as the moment at which the solution lost the transparency completely. The resultant gel was aged for 1 day at 60 °C. Then the solvent was disposed and the gel was gently dried at 60 °C. The macroscopic morphology of dried gels was characterized by scanning electron microscopy (SEM). Several dried gels were sintered to form silica glasses.

Figure 1 shows dependence of t_g and t_{ps} on y for gels of $x_1 = 1.9$. In all the systems, t_g decreased with an increase in y. t_{ps} was nearly equal or larger than t_g. In all the systems opaque gels were typically formed at $t_g \approx t_{ps}$ and at t_g of ca. 20–30 min. At a fixed y value, t_g decreased in the order of ammonium acetate, imidazole and ethylenediamine. Since pK_a of these amines are larger than that of ammonium acetate, the t_g decrease is probably due to an increase in pH and resultant promotion of the polycondensation. Thus, the amount of imidazole and ethyl-
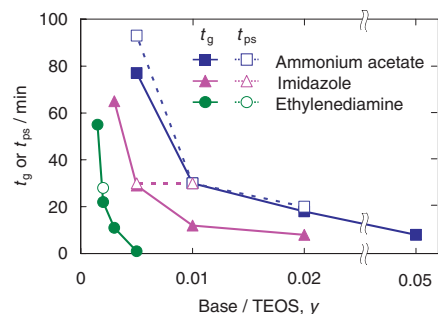

Figure 1. Variation of the gelation and phase separation times (t_g and t_{ps}, respectively) with the molar ratios of Brønsted bases (ammonium acetate, imidazole, and ethylenediamine) to TEOS, y, for gels prepared at $x_1 = 1.9$.
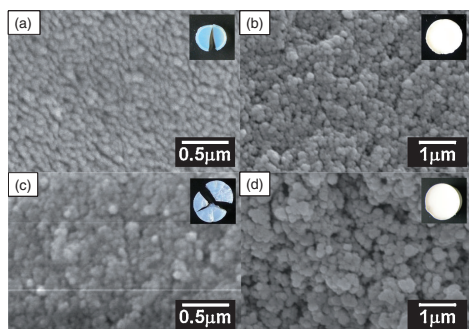
Figure 2. SEM images of dried gels prepared using 5.2 g of TEOS at $x_1 = 1.9$ from the ethylenediamine system with $y = 0.0015$ (a), $y = 0.002$ (b), and $y = 0.003$ (c), and the imidazole system with $y = 0.005$ (d). The insets show the appearance of these gels.
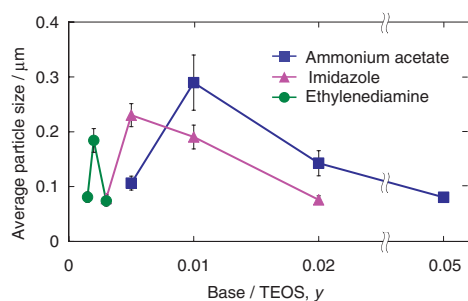

Figure 3. Compositional dependence of the average particle size of dried gels of $x_1 = 1.9$.

Figure 4. Absorption spectrum of a silica glass sample prepared from the ethylenediamine system at $x_1 = 1.87$ and $y = 0.002$ using 5.2 g of TEOS. The inset shows photograph of the glass sample and a dried gel prepared at the same condition.

enediamine (y) needed to obtain opaque gels is smaller than that for ammonium acetate. Figure 2 shows SEM images and photographs of dried gels prepared at $x_1 = 1.9$. The morphology is depicted as particle aggregates. The average particle sizes of opaque dried gels were ca. 0.1–0.2 μm both in the imidazole and ethylenediamine systems. These gels have macropores between the particles and can be dried easily without fracture. However, the particle size decreased both at the smaller and larger y sides, as typically seen in the ethylenediamine system (Figures 2a–2c). Dried gels with smaller particle sizes were semitransparent and often broken into smaller pieces during drying. Figure 3 summarizes the variation of the average particle size with y. In all the systems the particle size took a maximum against y. The decrease in the particle size at larger y is due to enhancement of the polycondensation, which increases viscosity and suppresses phase separation. At smaller y, on the contrary, the solution pH is likely to be too low to sufficiently slow down the hydrolysis after the second mixing. Thus, the silica oligomers turn hydrophilic and the phase separation is not induced.

A silica gel monolith obtained from the ethylenediamine system, where y was the smallest, was used to prepare a silica glass sample. A wet silica gel fabricated at $x_1 = 1.87$ and $y = 0.002$ using 5.2 g of TEOS was dried for 2 days. The resultant dried gel was sintered with a heating rate of $200\,°C\,h^{-1}$ up to $1300\,°C$ and maintained at that temperature for 1 h. The heating atmosphere was switched from air to helium at $600\,°C$. Figure 4 shows optical absorption spectrum and photograph of the resultant glass. The DUV absorption edge was located at ca. 160 nm, and it was mostly determined by residual SiOH groups.[18]
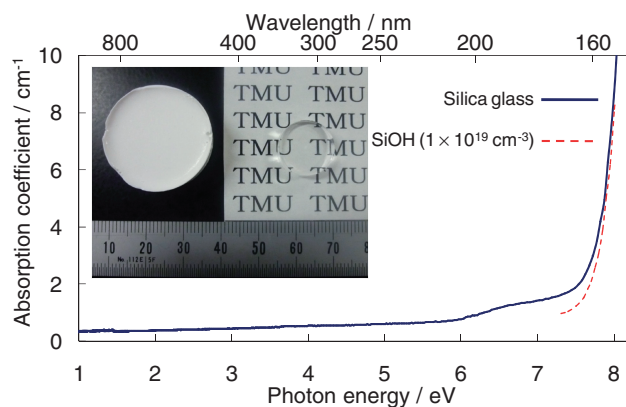
In conclusion, amines are useful as pH control agents in preparing macroporous silica gels utilizing macroscopic phase separation of tetraethoxysilane–water binary mixture. The driving force for the phase separation is exsolution of hydrophobic silica oligomers modified by unhydrolyzed ethoxy groups from hydrophilic solvent mixture. Imidazole and ethylenediamine are selected as amines that are expected to buffer the solution at neutral pH range, at which removal of the ethoxy groups is the slowest whereas polycondensation is enhanced. The molar fractions of imidazole and ethylenediamine required to obtain macroporous gels are ca. 1/2 and ca. 1/5 of that of ammonium acetate, which we used in previous studies. The resultant macroporous gels are dried easily without fracture and are converted to silica glasses with good visible and deep-ultraviolet transparency.

References
1 C. J. Brinker, G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel processing*, Academic Press, New York, **1990**.
2 S. S. Kistler, *J. Phys. Chem.* **1932**, *36*, 52.
3 M. Yamane, S. Aso, S. Okano, T. Sakaino, *J. Mater. Sci.* **1979**, *14*, 607.
4 M. Nogami, Y. Moriya, *J. Non-Cryst. Solids* **1980**, *37*, 191.
5 S. Wallace, L. L. Hench, *Mater. Res. Soc. Symp. Proc.* **1984**, *32*, 47.
6 T. Adachi, S. Sakka, *J. Mater. Sci.* **1987**, *22*, 4407.
7 T. Adachi, S. Sakka, *J. Non-Cryst. Solids* **1988**, *99*, 118.
8 F. Kirkbir, H. Murata, D. Meyers, S. R. Chaudhuri, A. Sarkar, *J. Sol-Gel Sci. Technol.* **1996**, *6*, 203.
9 H. Murata, D. E. Meyers, F. Kirkbir, S. R. Chaudhuri, A. Sarkar, *J. Sol-Gel Sci. Technol.* **1997**, *8*, 397.
10 K. Nakanishi, *J. Porous Mater.* **1997**, *4*, 67.
11 K. Nakanishi, N. Soga, *J. Am. Ceram. Soc.* **1991**, *74*, 2518.
12 H. Kaji, K. Nakanishi, N. Soga, *J. Sol-Gel Sci. Technol.* **1993**, *1*, 35.
13 H. Kozuka, S. Sakka, *Chem. Mater.* **1989**, *1*, 398.
14 K. Nakanishi, K. Kanamori, *J. Mater. Chem.* **2005**, *15*, 3776.
15 K. Kajihara, M. Hirano, H. Hosono, *Chem. Commun.* **2009**, 2580.
16 K. Kajihara, S. Kuwatani, R. Maehana, K. Kanamura, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1470.
17 C. J. Brinker, *J. Non-Cryst. Solids* **1988**, *100*, 31.
18 K. Kajihara, M. Hirano, L. Skuja, H. Hosono, *Phys. Rev. B* **2005**, *72*, 214112.